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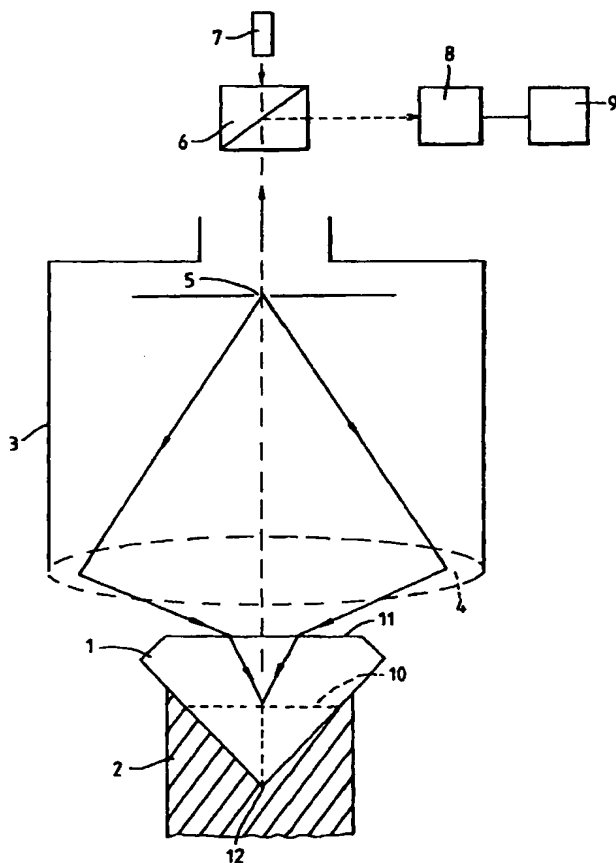
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(54) Title: **EXAMINING A DIAMOND**



(57) Abstract: In order to determine whether a blue-to-green diamond (1) has been artificially irradiated or ion bombarded to change its colour, it is irradiated with light of 633 nm wavelength in order to stimulate the emission of luminescence, and luminescence from about 680 to about 800 nm is detected using a confocal microscope (3) and a spectrometer (8) as the focal plane (9) is scanned vertically through the diamond (1). A rapid decrease in luminescence with increase in depth indicates natural irradiation whilst a more rapid decrease indicates ion bombardment. Alternatively, in order to determine whether a diamond (1) is a natural/synthetic doublet, it is irradiated with radiation of 325 nm wavelength in order to stimulate the emission of luminescence, and luminescence from 330 to 450 nm is detected. An abrupt change in luminescence with increase in depth indicates that the diamond is a natural/synthetic doublet.

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Examining a Diamond

Background of the Invention

The present invention relates to an apparatus for examining a diamond, primarily for detecting whether the diamond has been artificially irradiated or ion bombarded to change its colour or whether the diamond is a natural/synthetic doublet.

Natural green diamonds owe their colour to irradiation by naturally occurring radio isotopes which produce alpha-particles, when the radio isotopes are adjacent the diamond in the ground. The alpha-particles penetrate only to a depth of about 30 μm below the surface of the diamond and create radiation damage to the diamond lattice, principally in the form of lattice vacancies. The vacancies give rise to a characteristic vibronic absorption system in the red end of the visible spectrum, giving rise to a blue-to-green coloration.

However, artificial irradiation or ion bombardment (ion implantation) can be used to produce a blue-to-green colour in diamonds. This treatment is usually applied to polished diamonds but the treatment can be applied to rough diamonds. Artificial irradiation is usually carried out using high-energy electrons, which have a penetration depth in diamond of a few millimetres, considerably more than that of alpha-particle irradiation, or using fast neutrons, which have a penetration depth in diamond of a few centimetres, very considerably more than that of alpha-particle irradiation. High energy ions used for ion bombardment typically have a penetration depth of about 1 μm in diamond, considerably less than that of natural alpha-particle irradiation. Hitherto, in order to be certain whether a rough or polished blue-to-green diamond had been naturally or artificially irradiated, it was necessary to destructively cross-section the diamond and observe the depth of penetration of the colour below the surface.

Because naturally irradiated diamond gemstones can command a higher price than diamonds that owe their colour to artificial irradiation or ion bombardment, a suitable method of testing is required for the sake of consumer confidence.

Natural/synthetic doublets can be made by depositing synthetic diamond on a natural diamond, normally in its polished or part-processed state, to form part of the crown or pavilion of the doublet. There are techniques for detecting whether the diamond is a doublet - see for instance WO 94/20837, WO 95/20152, WO 96/07895, WO 96/07896, WO 97/04302 and WO 97/04303. These techniques are unsatisfactory because they cannot be automated and/or require expensive components.

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior techniques, or to provide a useful alternative.

It is generally desirable to be able to examine automatically, and to provide a technique which can be used for loose diamonds or diamonds set in jewellery.

The Invention

In its broadest aspect, the present invention provides apparatus as set forth in Claim 1 or 22 and methods as set forth in Claim 23 or 24. The remaining Claims set forth preferred or optional features of the invention.

In general terms, any change in the material of which the diamond is composed may be detected. However, the method is primarily used for detecting whether the diamond has been artificially irradiated or ion bombarded to change its colour, or for detecting whether the diamond is a natural/synthetic doublet. It would be possible to have a dual-purpose apparatus incorporating two different irradiating means for irradiating at different wavelengths; the luminescence detecting means for the two different purposes would be very similar, but the comparing means would be different.

Any characteristic of luminescence can be compared, but preferably the intensity of a spectral feature of the luminescence is compared. The luminescence detected can

be normalised by ratioing it with a luminescence emission characteristic of all diamonds, preferably Raman. This normalisation procedure allows results to be corrected for changes in collection efficiency or size of stone.

If the diamond has been artificially irradiated with high-energy electrons or fast neutrons to change its colour, the decrease in the luminescence detected with depth is less rapid than the decrease with depth in the case of a diamond which has been naturally irradiated. This is discussed in more detail hereafter in relation to Figures 4a, 4b and 5 of the accompanying drawings.

If high-energy ion bombardment is used, the decrease of luminescence detected with depth is more rapid than in the case of a diamond which has been naturally irradiated. In practice, the same irradiation wavelength and comparing means can be used to detect both artificial irradiation (in effect at one end of the scale) and ion bombardment (in effect at the other end of the scale), and therefore can indicate on a screen whether the diamond has been artificially irradiated or whether the diamond has been ion bombarded. The difference between treatment with high-energy electrons, which have a penetration depth of a few millimetres, and fast neutrons, which have a penetration depth of a few centimetres, can be detected, but only for diamonds more than 2 to 3 mm deep.

Although the irradiation or ion bombardment detection is directed primarily at rough diamonds, the method of the invention can also be used to identify artificially irradiated or ion bombarded polished diamonds. When a naturally irradiated stone is polished, the shape of the stone is changed and the depth of irradiated material is no longer uniform. In the case of a polished diamond that has been artificially irradiated or ion bombarded subsequent to being polished, if the change in intensity of luminescence with depth is measured from a number of points on the diamond it will be found to be uniform with respect to the polished surface, clearly indicating that the irradiation is artificial.

To detect artificial irradiation or ion bombardment, the N3 zero-phonon line cannot be used as there is no systematic change in the line. However, stimulating

radiation of any wavelength capable of causing luminescence from the GR1 optical centre can be used. The GR1 (General Radiation 1) system is a spectroscopic feature of diamond, which has a principle sharp line at 741 nm, due to an electronic transition at a vacancy centre in diamond. The absorption analogue of this system gives rise to the blue-to-green coloration. If the GR1 optical centre is excited at room temperature with light in the wavelength range 500 to 740 nm, it produces luminescence with a strong line at 741 nm. Thus, the stimulating radiation is preferably radiation of about 500 to about 740, for instance about 633, nm wavelength, and luminescence including wavelengths from about 740 to about 745 nm is detected.

If the diamond is a doublet, there is a change in the luminescence when the detection reaches the depth where the change between natural and synthetic, or vice versa, occurs.

To detect doublets, the GR1 optical centre cannot be used, but a change in the N3 zero-phonon line can be detected. The stimulating irradiation is preferably radiation of about 300 to about 400, for instance about 325, nm wavelength and luminescence from about 330 to about 450 nm is detected. However a change in the rate of decrease of the Raman signal with depth, due to differential absorption of the stimulating irradiation, could alternatively be used to indicate a change in material of which the diamond is composed.

The whole procedure is automated. The technique can be used to detect artificial irradiation or ion bombardment in diamonds much less than about 10 points (0.1 carats) in weight, although they are preferably at least 1 mm deep. The invention can be used for doublet detection in diamonds down to about ten points (0.1 carats) in weight, and possibly less.

If stimulating radiation capable of penetrating the whole depth of the diamond is focused within the depth of the diamond, the luminescence from different depths can be detected, e.g. by substantially preventing detection of luminescence which is not substantially in the focal plane. A suitable technique is a confocal technique, using a confocal spectrometer. A confocal aperture placed at the back-focal plane of a microscope ensures that only luminescence from the focal point of the objective reaches

the spectrometer detector. Luminescence from other parts of the sample fails to pass through the confocal aperture and so is not detected. The area of the selected region depends upon the diameter of the confocal aperture and the magnification of the microscope objective. The luminescence is collected from a volume effectively comprised of the selected area, determined by the confocal aperture diameter and objective magnification, and the depth of focus of the objective, determined by its numerical aperture.

Although the method is normally carried out at room temperature, a lower temperature may be used by employing a cryostat such as the Microstat N from Oxford Instruments.

The Drawings

The invention will be further described, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a schematic vertical cross-section through apparatus in accordance with the invention, showing a polished diamond being examined in accordance with the method of the invention;

Figure 2 is a block diagram of the apparatus of Figure 1;

Figure 3 is a flow chart illustrating software in the apparatus of Figure 1;

Figure 4a shows GR1 luminescence spectra at the surface and at depth increments of 10 μm below the surface of a rough naturally alpha-irradiated diamond;

Figure 4b corresponds to Figure 4a, but shows the normalised integrated intensity of the GR1 luminescence ;

Figure 5 corresponds to Figure 4b, but the diamond is an artificially electron-irradiated diamond;

Figure 6 corresponds to Figures 4b and 5, but the diamond is an artificially ion-implanted diamond;

Figure 7 is a photoluminescence/Raman spectrum of a typical type Ia natural diamond;

Figure 8 corresponds to Figure 7, but the diamond is CVD (chemical vapour deposited) diamond;

Figure 9a is the depth profile of the normalised integrated N3 luminescence intensity for a first doublet, the distance being the distance moved by the diamond doublet;

Figure 9b corresponds to Figure 9a, but the depth is the distance moved by the focal plane within the diamond doublet;

Figure 10a is the depth profile of the normalised integrated N3 luminescence intensity for a second diamond doublet, the distance moved being the distance moved by the diamond doublet; and

Figure 10b corresponds to Figure 10a, but the depth moved is the distance moved by the focal plane within the diamond doublet.

Figure 1

Figure 1 shows a polished diamond 1, for convenience. However, the diamond 1 could be a rough diamond or a sawn half – a rough diamond could be supported by an easily deformable material such as “Blu-Tak”. There may be practical limitations regarding the surface texture of rough diamonds or sawn halves, and consequent irradiation scattering, but otherwise the technique is equally applicable to rough diamonds or sawn halves and to polished diamonds. The precise location of the surface is not determined physically but by the change in the detected luminescence. The diamond 1 is placed on a mount or stage 2 below a confocal microscope 3, the stage 2

being normal to the optical axis. The stage 2 shown is designed to receive the culet of a polished diamond 1, but it could be designed for a standard piece of jewellery such as a finger ring; alternatively a piece of jewellery could be held by an easily deformable material, as above. Normally, the table of the diamond 1 should be exposed and be normal to the optical axis. Though not illustrated, the stage 2 is carried on a table which can be moved up and down by a stepping motor. The microscope 3 has an objective lens 4 and a confocal aperture 5. Above the microscope 3, there is a beam splitter 6, a laser 7 for irradiating the diamond 1, a spectrometer 8, and a processor 9. All the parts are illustrated extremely schematically.

The confocal aperture 5 prevents light from outside the focal region entering the spectrometer 8. The instantaneous focal plane is indicated at 10 and the arrangement is such that the focal plane 10 can be scanned right through the diamond from the topmost point (here the table 11) to the bottommost point (here the culet 12). Scanning is most conveniently done by moving the stage 2 vertically, in predetermined intervals, say of 10 μm or 100 μm . The laser beam is refracted as it enters the diamond 1 and therefore the distance travelled by the focal point of the laser (within the diamond 1) at a wavelength of e.g. 633 nm is approximately 2.41 times greater than the distance travelled by the diamond 1 itself (2.41 is the refractive index of diamond at 633 nm), or approximately 2.51 times greater at a wavelength of 325 nm (2.51 is the refractive index of diamond at 325 nm).

Figure 2

The block diagram of Figure 2 shows items 3 to 8 as a confocal spectrometer associated with a microscope 13 and having a CCD detector 14 for detecting the luminescence (in effect, part of the spectrometer 8). The processor 9 is shown with a monitor 15 for displaying the detected results. The stage 2 is shown as an xyz stage carrying a matrix 2a of diamond samples (say 5 x 5), the x, y movements (in the horizontal plane) being for enabling one diamond of the matrix of samples 2a to be positioned beneath the microscope 13. The z movement is the vertical movement discussed above.

Figure 3

The flow chart of Figure 3 is in general self-explanatory and is not further described in detail. The stage "Process data" includes analysing the rate of change of luminescence with depth in order to identify an interface or change in material.

Examples of Artificial Irradiation and Ion Bombardment Detection

In one suitable apparatus, the laser 7 is a He-Ne laser having a 10-20 mW output at 633 nm. The laser 7 can be supplied together with the confocal microscope 3 and the spectrometer 8 as a LabRam Infinity Confocal Spectrometer, manufactured by J Y Horiba. Luminescence from about 680 to about 800 nm is detected. In diamond this system enables depths of 0 to 500 μm to be probed using a x100 objective lens 4 and a 50 μm confocal aperture 5. Depths of 0 to 10 mm may be probed using a x20 objective lens 4 and a 200 μm confocal aperture 5.

When using the apparatus, the step "Process data" of Figure 3 is as follows:

The profile of the Raman normalised integrated intensity of the GR1 zero-phonon-line versus depth below the sample surface is analysed.

If a significant decrease in the above parameter is observed at a depth of less than 10 microns, then the diamond is identified as potentially 'Ion bombarded'.

If a significant decrease in the above parameter is observed at a depth of 500 to 2000 microns, then the diamond is identified as potentially 'Electron Irradiated'.

If no significant decrease in the above parameter is observed over depths greater than 2000 microns, then the diamond is identified as potentially 'Neutron Irradiated'.

If a significant decrease in the above parameter is observed at a depth of 15 to 35 microns, then the diamond is identified as 'Naturally Irradiated'.

The depth at which the significant decrease occurs may be determined by differentiating the signal and determining where the minimum lies using standard mathematical algorithms. The shape of the profile may be compared with the expected shape by reference to stored profile reference files.

Figures 4a, 4b and 5

Figure 4a shows a photoluminescence/Raman spectrum recorded using the confocal spectrometer with the x100 objective lens 4 and 50 μm confocal aperture 5. The lines in Figure 4a are referenced with the depth below the surface, the line O being as recorded at the surface. The diamond Raman line is at approximately 691 nm and is shown by a sharp intensity peak. The normalisation of Figure 4b was achieved by ratioing the integrated GR1 luminescence intensity against the integrated intensity of the diamond Raman line. If the Raman signal falls to less than 10 per cent of its initial value, it can be assumed that the focal point of the probe is no longer within the diamond. By choosing the appropriate grating, CCD detector and central wavelength position of the spectrometer grating (in the spectrometer 8), both the GR1 and Raman signals may be captured within the same spectrum. Software, such as that provided with the LabRam Infinity confocal spectrometer, was configured to provide a real-time display of the depth profile. The processor 9 has suitable software to indicate automatically whether the diamond has been naturally or artificially irradiated.

The centre of the surface of the table of the diamond 1 was first positioned at the focal point of the laser beam and spectra were recorded at 10 μm intervals as the diamond 1 was moved upwards towards the objective lens 4 that focused the laser. This process was equivalent to collecting spectra as the focal point of the laser was scanned into the diamond 1 via the table.

As can be seen from Figure 4b, for the naturally alpha-irradiated diamond, the GR1 luminescence was substantially confined to within 30 μm of the surface whereas (as shown in Figure 5) for the artificially electron-irradiated diamond, the GR1 luminescence is significantly intense over 1 mm below the surface (the different scales of Figures 4b and 5 should be noted).

Figure 6

Figure 6 shows the normalised integrated intensity curve for an ion bombarded diamond, the profile differing from that of Figures 4b and 5, as well as the scales being very different, the depth of implantation being very low.

A graph of the normalised integrated intensity of the GR1 luminescence for a neutron bombarded diamond would be a horizontal line, again differing from the spectra of Figure 4b, and Figure 5.

Examples of Doublet Detection

In one suitable apparatus, the laser 7 is a He-Cd laser having a 10-100 mW output at 325 nm. The laser 7 can be supplied together with the confocal microscope 3 and the spectrometer 8 as a LabRam Infinity Confocal Spectrometer, manufactured by J Y Horiba. Luminescence from about 330 to about 450 nm is detected. In diamond, this system enables depths of 0 to 500 μm to be probed using a x100 objective and a 50 μm confocal aperture 5. Depths of 0 to 10 mm may be probed using a x20 objective and a 200 μm confocal aperture 5.

By choosing the appropriate grating, CCD detector and central wavelength position of the spectrometer grating (in the spectrometer 8), both the N3 and Raman signals may be captured within the same spectrum. Software, such as that provided with the LabRam Infinity confocal spectrometer, was configured to provide a real-time display of the depth profile.

The processor 9 has suitable software to indicate automatically whether the diamond is a doublet. In the step "Process data" of Figure 3, the software normalises the integrated intensity of the N3 zero-phonon line relative to the integrated intensity of the diamond Raman line. The profile of the Raman normalised integrated intensity of the N3 zero-phonon-line versus depth below sample surface is analysed. If a significant decrease or increase in the above parameter is observed, then the diamond will be referred as a possible doublet. If the profile is broadly flat (and non-zero) then the

diamond will be passed as a 'non-doublet'. As above, if the Raman signal falls to less than 10 per cent of its initial value, it can be assumed that the focal point of the probe is no longer within the diamond.

Figure 7

Figure 7 is a typical photoluminescence/Raman spectrum for type Ia natural diamond, collected confocally at room temperature with 325 nm He-Cd laser excitation. It contains the N3 zero phonon line at 415 nm with associated vibronic structure at longer wavelengths. More than 95% of all natural diamonds have the N3 zero phonon line; those that do not are selected out beforehand. The spectrum also contains the Raman line at approximately 339 nm, shown as a sharp intensity peak.

Figure 8

Figure 8 is a similar spectrum for CVD synthetic diamond. It does not contain the N3 zero phonon line at 415 nm or its associated vibronic structure.

Figures 9a and 9b

Figures 9a and 9b show the measured confocal depth profiles of normalised N3 luminescence for a first doublet, which was produced for experimental purposes only. The first doublet was a round brilliant, partly composed of natural type Ia diamond and partly of CVD synthetic diamond. It has a CVD synthetic diamond crown and the interface between this component and the natural diamond component was known to be 0.86 mm below the table, the total depth of the stone being 3.19 mm.

The centre of the surface of the table of the doublet 1 was first positioned at the focal point of the laser beam and spectra were recorded at 100 μm intervals as the doublet 1 was moved upwards towards the objective lens 4 that focused the laser. This process was equivalent to collecting spectra as the focal point of the laser was scanned into the doublet 1 via the diamond table.

As explained above, the distance travelled by the focal point of the laser within the stone is approximately 2.51 times greater than the distance travelled by the stone itself. In Figure 9a, the horizontal-axis is the distance travelled by the stone from the position in which the table is at the focal point of the laser. In Figure 9b, the horizontal-axis is this distance multiplied by 2.51. This corresponds approximately to the depth of the focal point of the laser beam below the diamond table.

The change in the graph of Figures 9a and 9b is not abrupt because of the relatively poor resolution at the depths that are being probed, and the intervals between measurements. However the precise depth of the interface is not usually of concern, only whether or not there is an interface.

Figures 10a and 10b

Figures 10a and 10b correspond closely to Figures 9a and 9b, but show the spectra for a second doublet, which was also produced for experimental purposes only. The second doublet was a round brilliant, partly composed of natural type Ia diamond and partly of CVD diamond. It has a natural type Ia diamond crown and the interface between this component and the CVD synthetic diamond component is 0.75 mm below the table, the total depth of the stone being 1.64 mm.

The second doublet was positioned as for the first doublet of Figures 9a and 9b.

x x x

Unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', and the like, are to be construed in an inclusive as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

The present invention has been described above purely by way of example, and modifications can be made within the spirit of the invention.

CLAIMS:

1. Apparatus for automatically indicating a change in material within a diamond, comprising:
 - means for irradiating the diamond to stimulate the emission of luminescence;
 - means for automatically detecting the luminescence at different depths within the diamond;
 - means for automatically comparing the luminescences so detected and thereby detecting a change in the material of which the diamond is composed; and
 - means responsive to said comparing means for automatically indicating said change in material.
2. The apparatus of Claim 1, wherein the intensity of a spectral feature of the luminescence is detected and compared.
3. The apparatus of Claim 1 or 2, wherein the detecting means are arranged such that the depth at which luminescence is detected moves automatically by fixed increments.
4. The apparatus of any of the preceding Claims, wherein the comparing means include software for analysing the rate of change of luminescence with depth in order to identify an interface or change in material.
5. The apparatus of any of the preceding Claims, wherein the stimulating irradiation is capable of penetrating the whole depth of the diamond but is focused within the depth of the diamond, and the luminescence is sensed by collecting luminescence from said different depths.
6. The apparatus of Claim 5, carried out using a technique which substantially prevents detection of luminescence which is not in the focal plane at said depth.
7. The apparatus of Claim 5, and carried out using a confocal technique.

8. The method of Claim 5, and carried out using a confocal spectrometer.
9. The apparatus of any of the preceding Claims, wherein the luminescence detected is normalised by ratioing it with a luminescence emission characteristic of all diamonds.
10. The apparatus of Claim 9, wherein said characteristic luminescence emission is Raman.
11. The apparatus of any of the preceding Claims, and arranged to indicate whether the diamond has been artificially irradiated to change its colour, the indicating means indicating whether the diamond has been artificially irradiated.
12. The apparatus of any of the preceding Claims, and arranged to indicate whether the diamond has been ion bombarded to change its colour, the indicating means indicating whether the diamond has been ion bombarded.
13. The apparatus of any of the preceding Claims, wherein the irradiating means cause luminescence from the GR1 optical centre.
14. The apparatus of any of the preceding Claims, wherein the stimulating irradiation is irradiation of about 500 to about 740 nm wavelength.
15. The apparatus of Claim 14, wherein the stimulating irradiation is irradiation of about 633 nm wavelength.
16. The apparatus of any of the preceding Claims, wherein luminescence from about 680 to about 800 nm is detected.
17. The apparatus of any of the preceding Claims, and arranged to indicate whether the diamond is a natural/synthetic doublet.

18. The apparatus of any of Claims 1 to 10 and 17, wherein the irradiating means cause luminescence at the N3 optical centre to give rise to the N3 zero-phonon line.
19. The apparatus of any of Claims 1 to 10 and 17, wherein the stimulating irradiation is irradiation of about 300 to about 400 nm wavelength.
20. The apparatus of Claim 19, wherein the stimulating irradiation is irradiation of about 325 nm wavelength.
21. The apparatus of Claim 19 or 20, wherein luminescence from about 330 to about 450 nm is detected.
22. Apparatus for examining a diamond, substantially as herein described with reference to Figures 1 to 3 of the accompanying drawings, or substantially as herein described in any of the preceding Examples.
23. A method of examining a diamond in order to detect whether there is a change in material within the diamond, comprising using the apparatus of any of Claims 1 to 21, whereby the change in material is automatically indicated.
24. A method of examining a diamond in order to determine whether there is a change in material within the diamond, substantially as herein described with reference to any of Figures 1 to 3, Figures 4a, 4b and 5, Figures 9a and 9b and Figures 10a and 10b, or in the foregoing Examples.

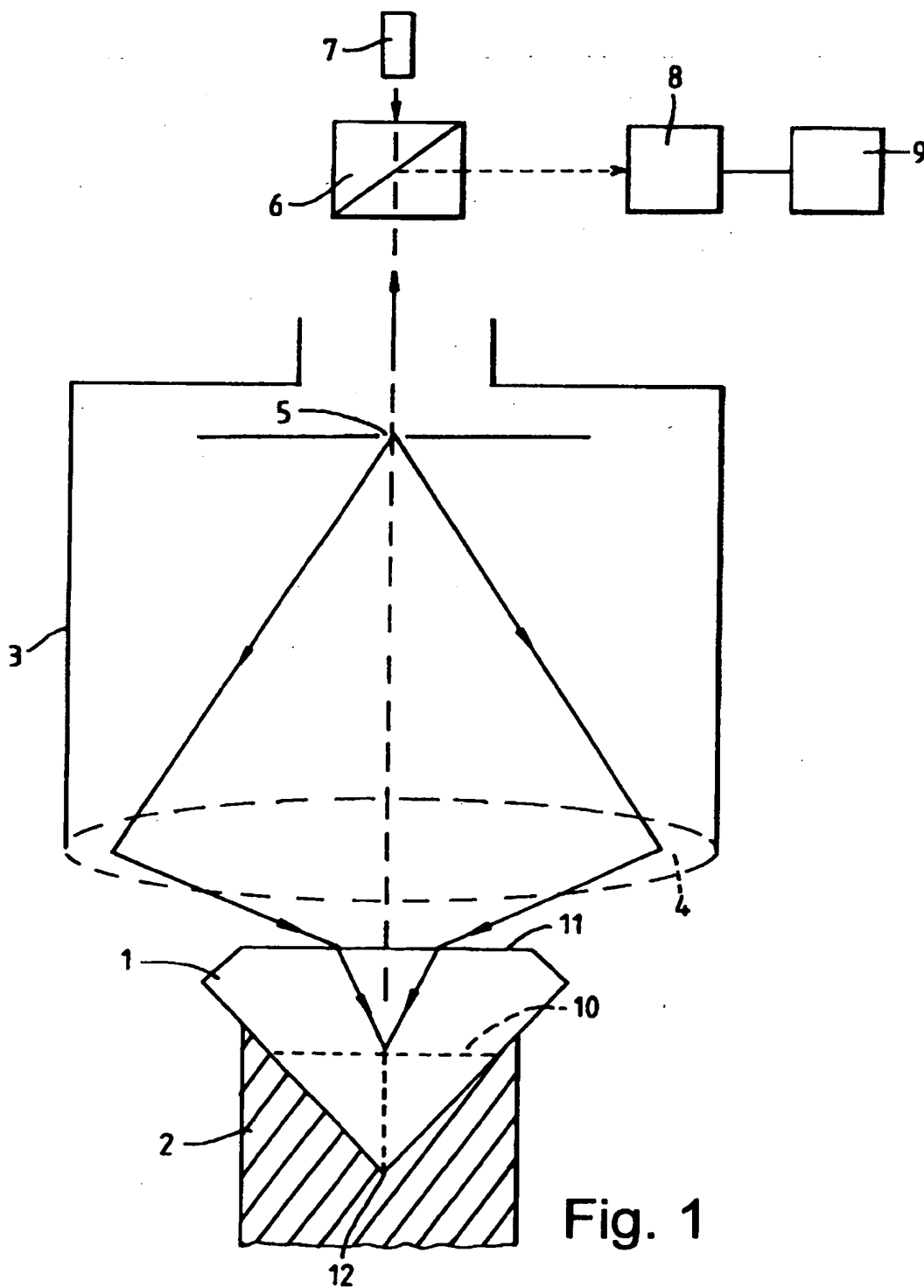


Fig. 1

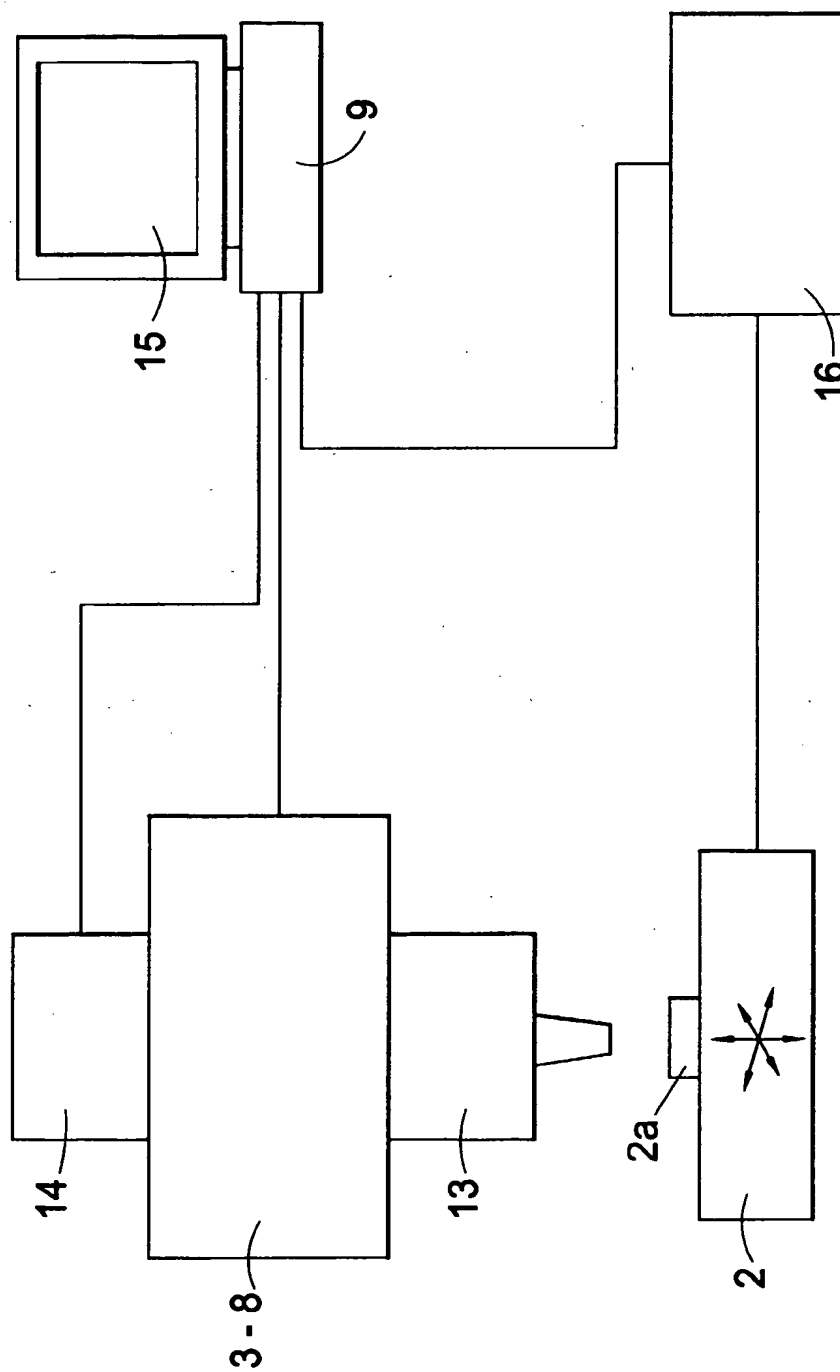
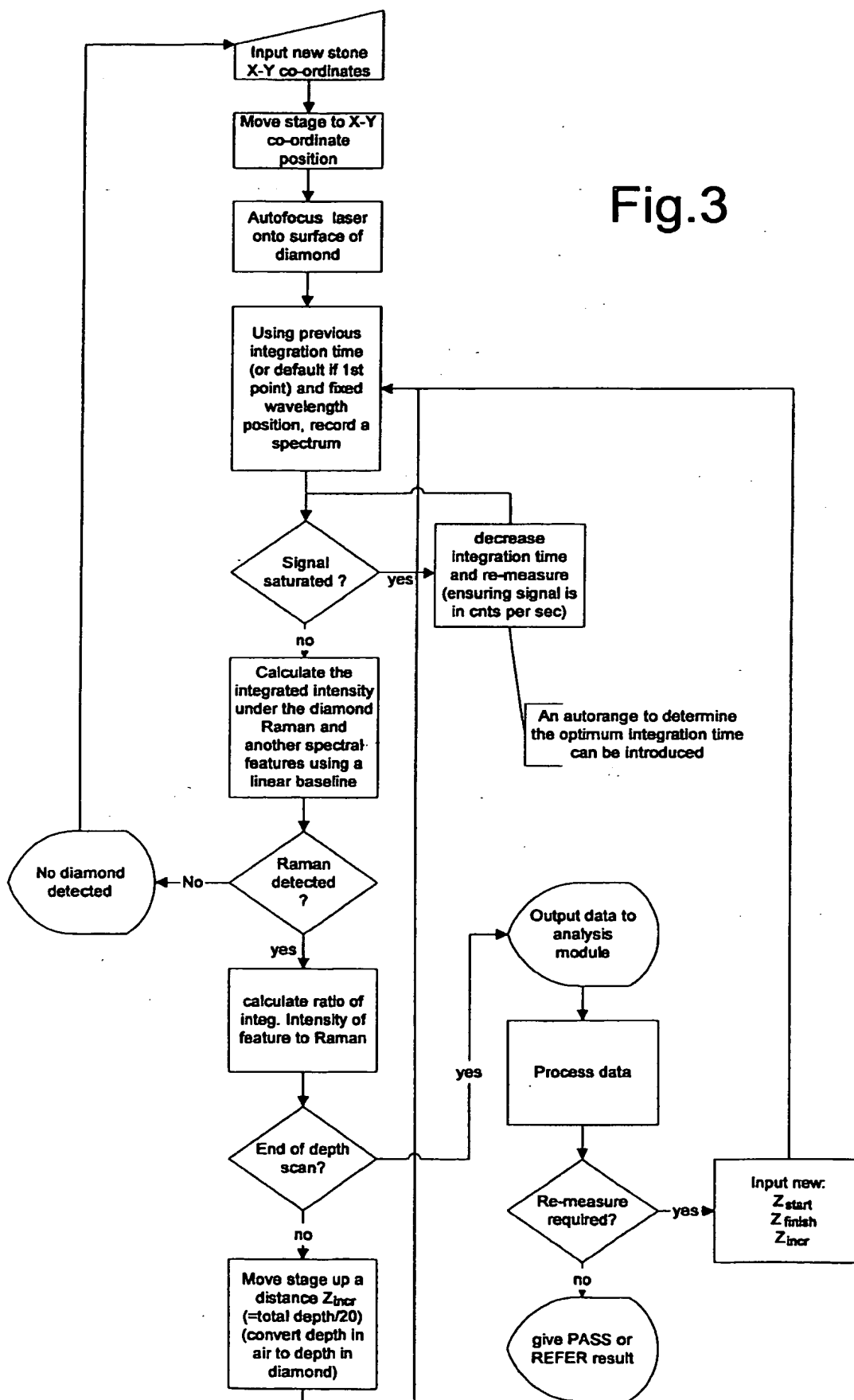


Fig.2

Fig.3



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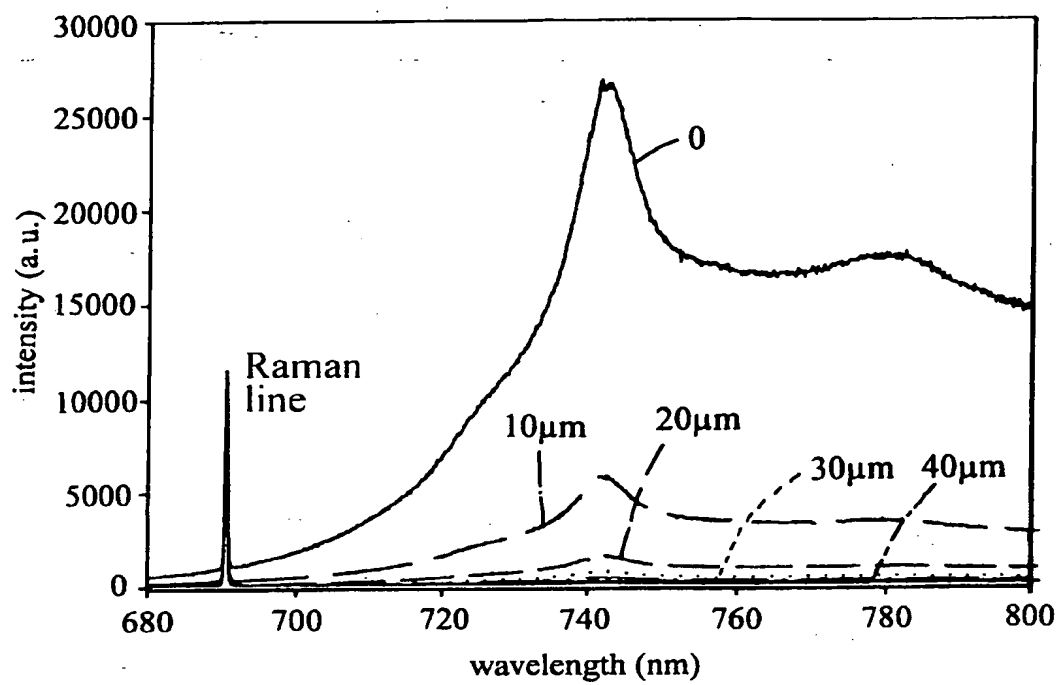


Fig.4a

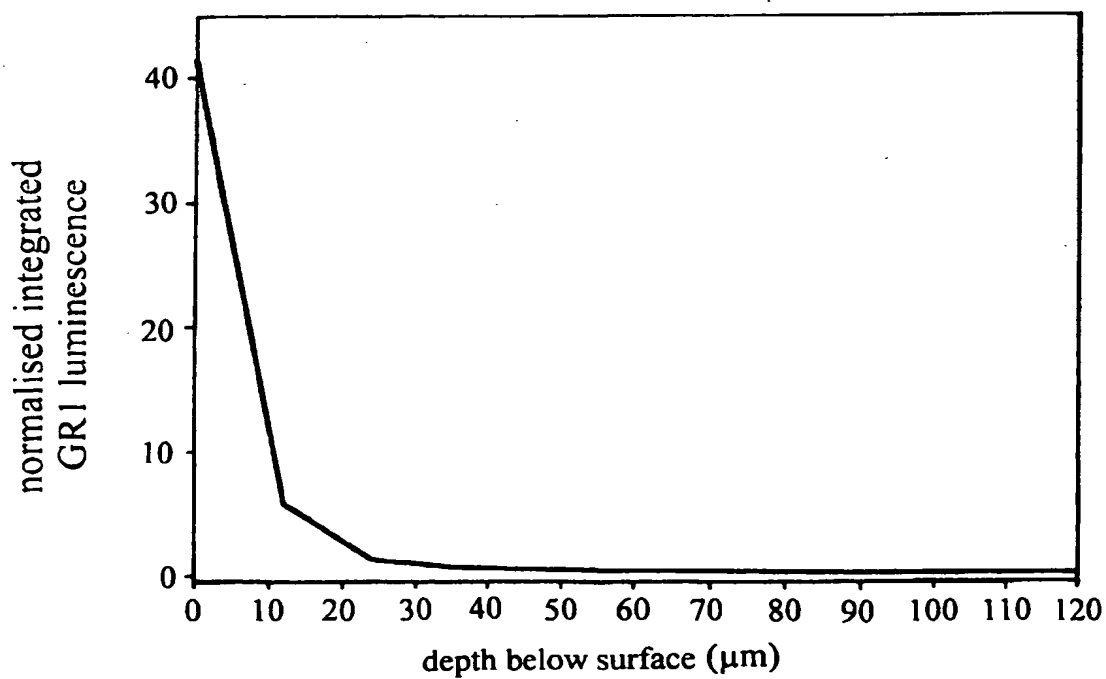


Fig.4b

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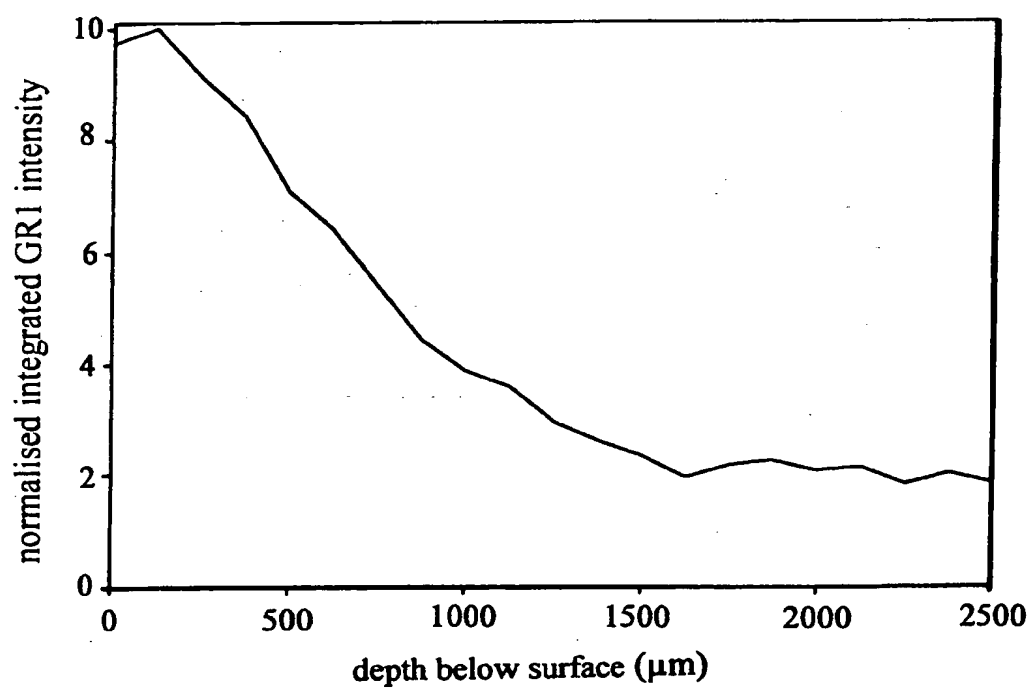


Fig.5

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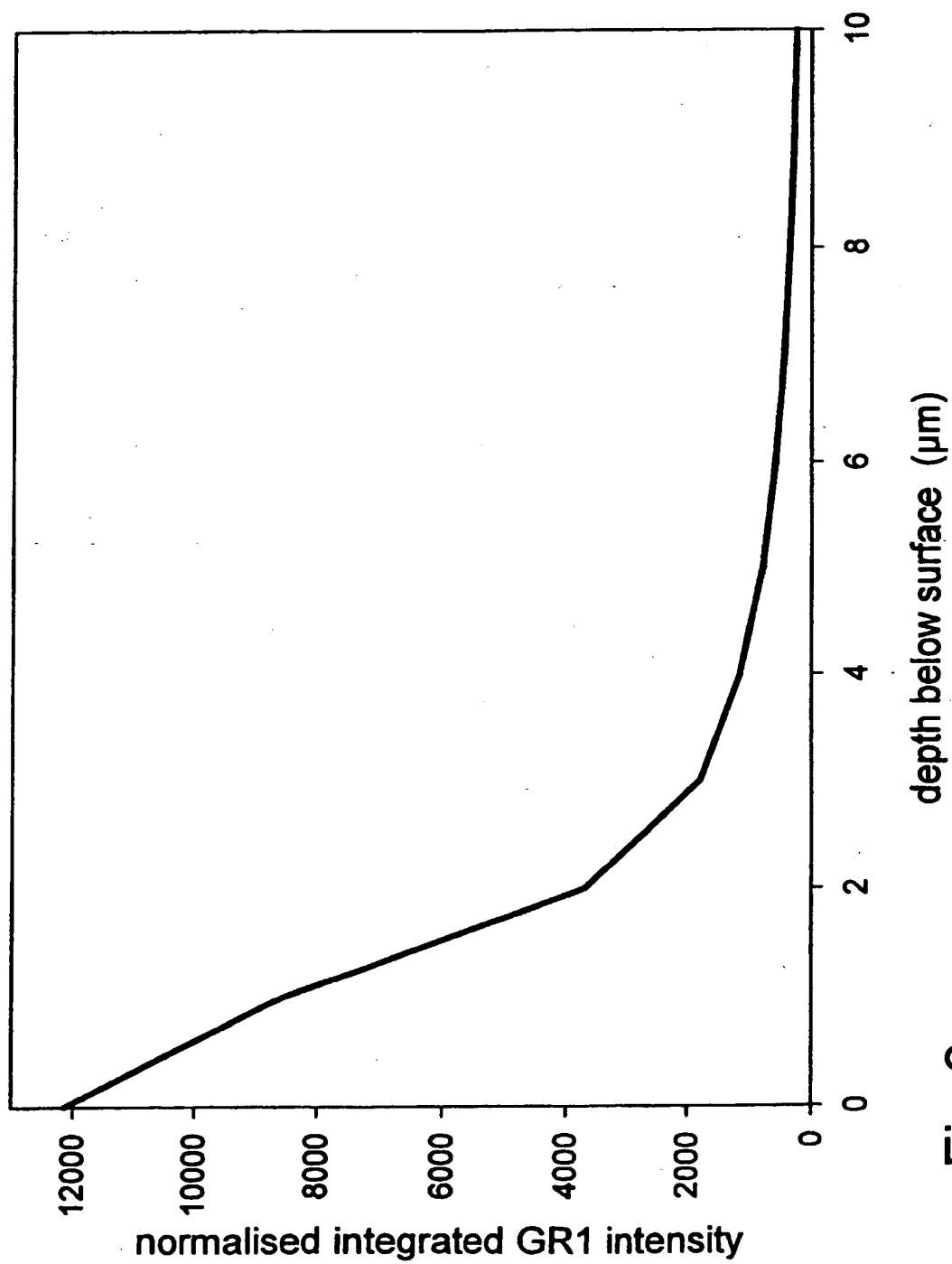


Fig.6

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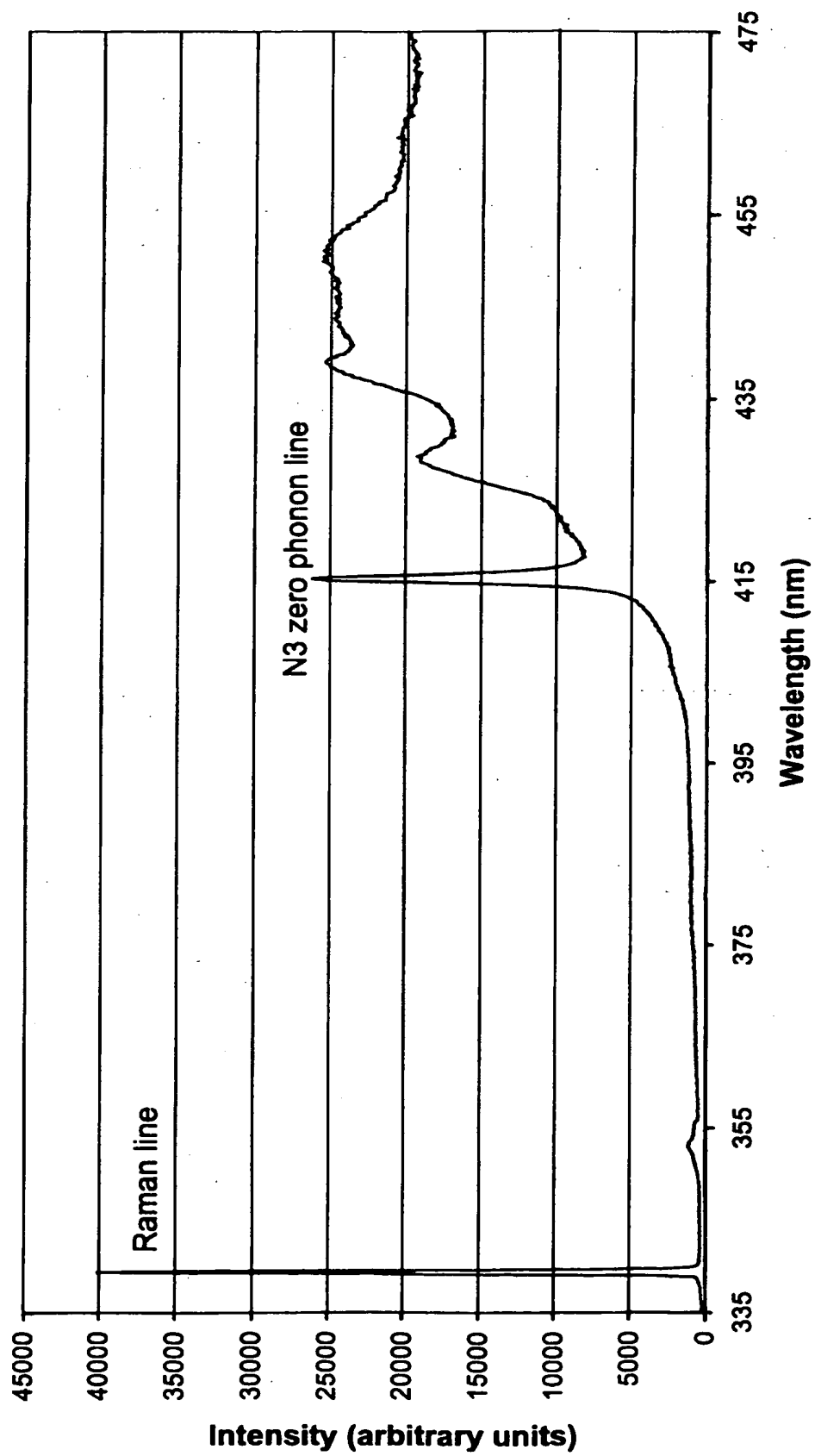


Fig.7

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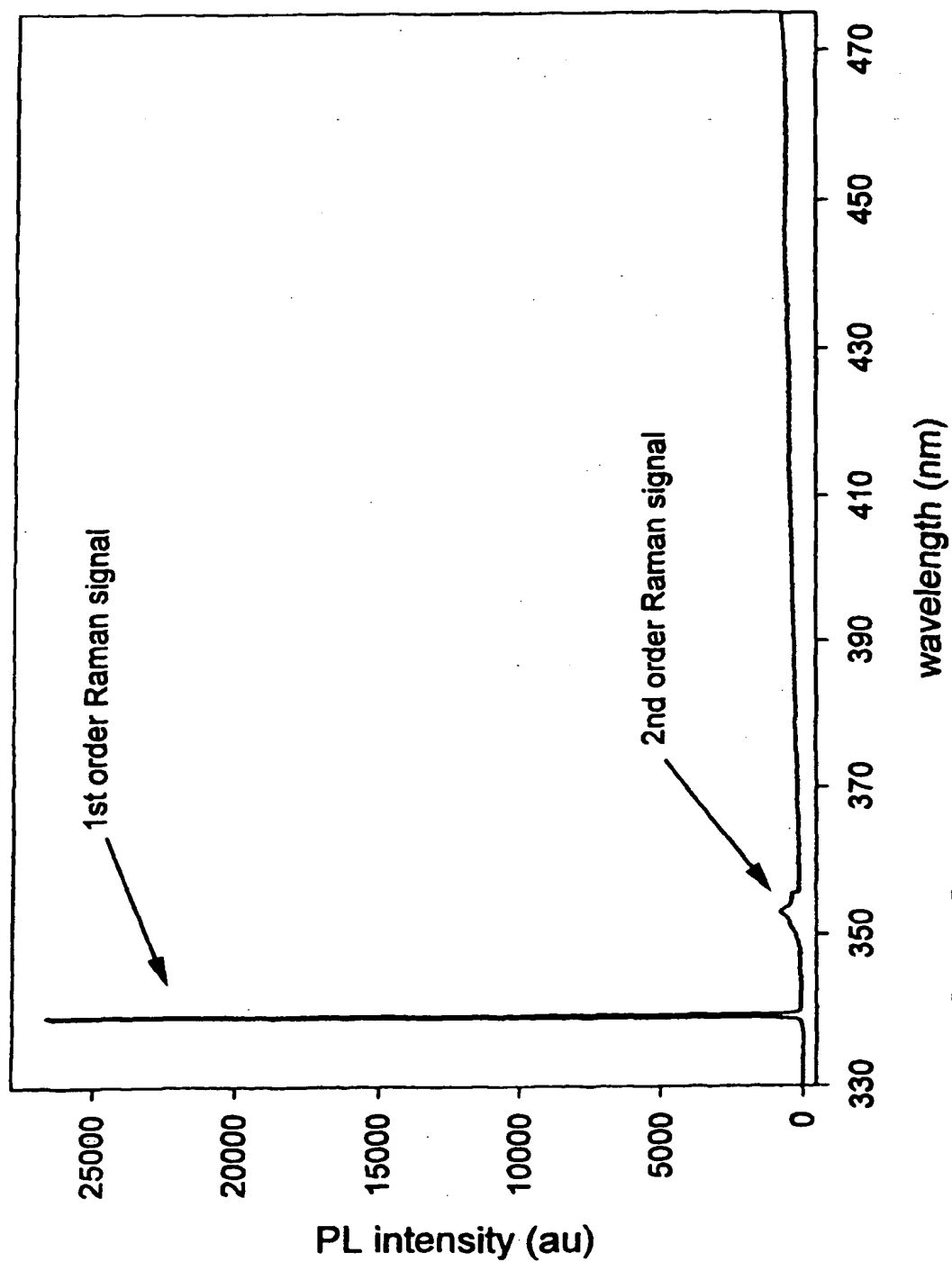


Fig.8

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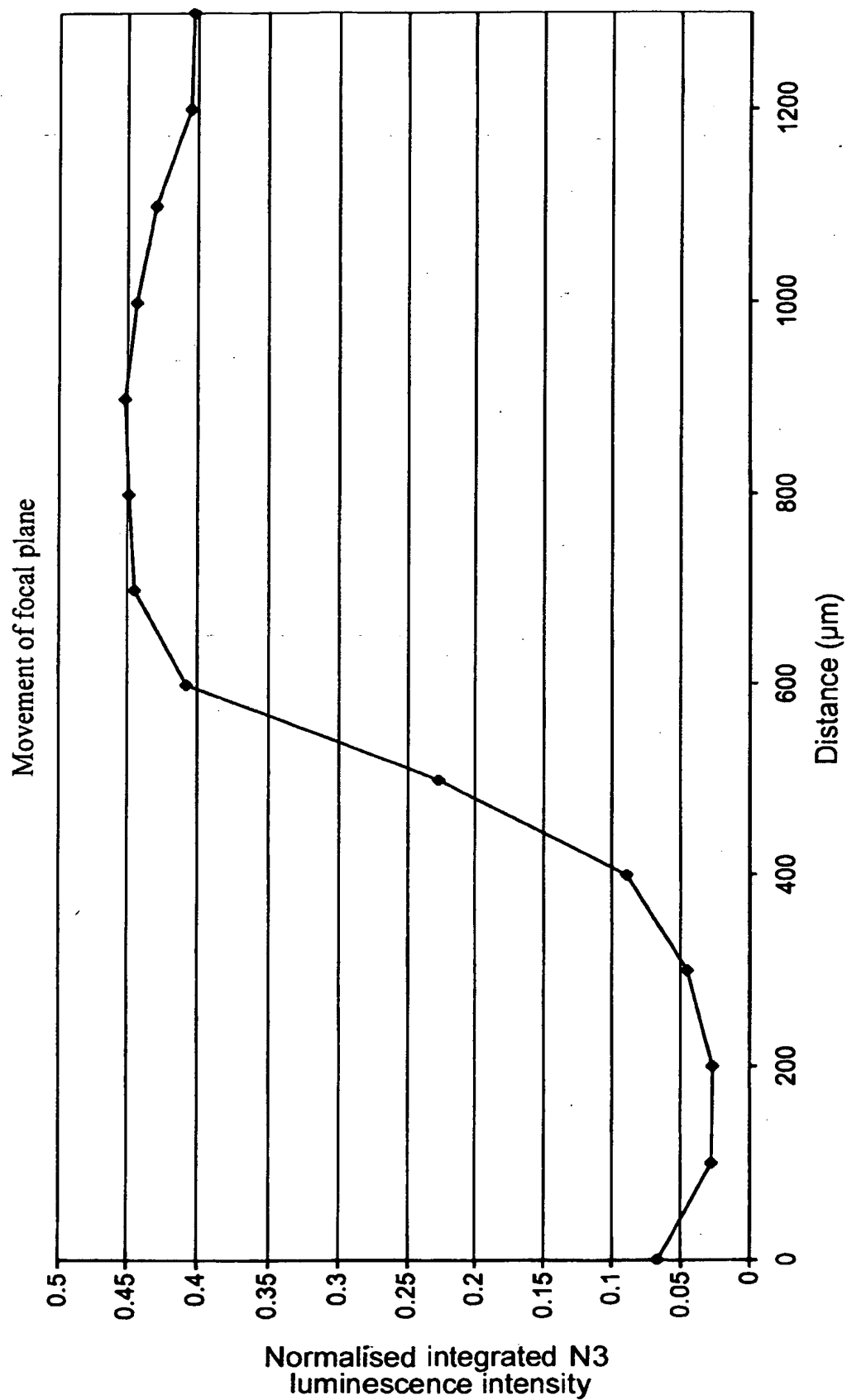


Fig.9a

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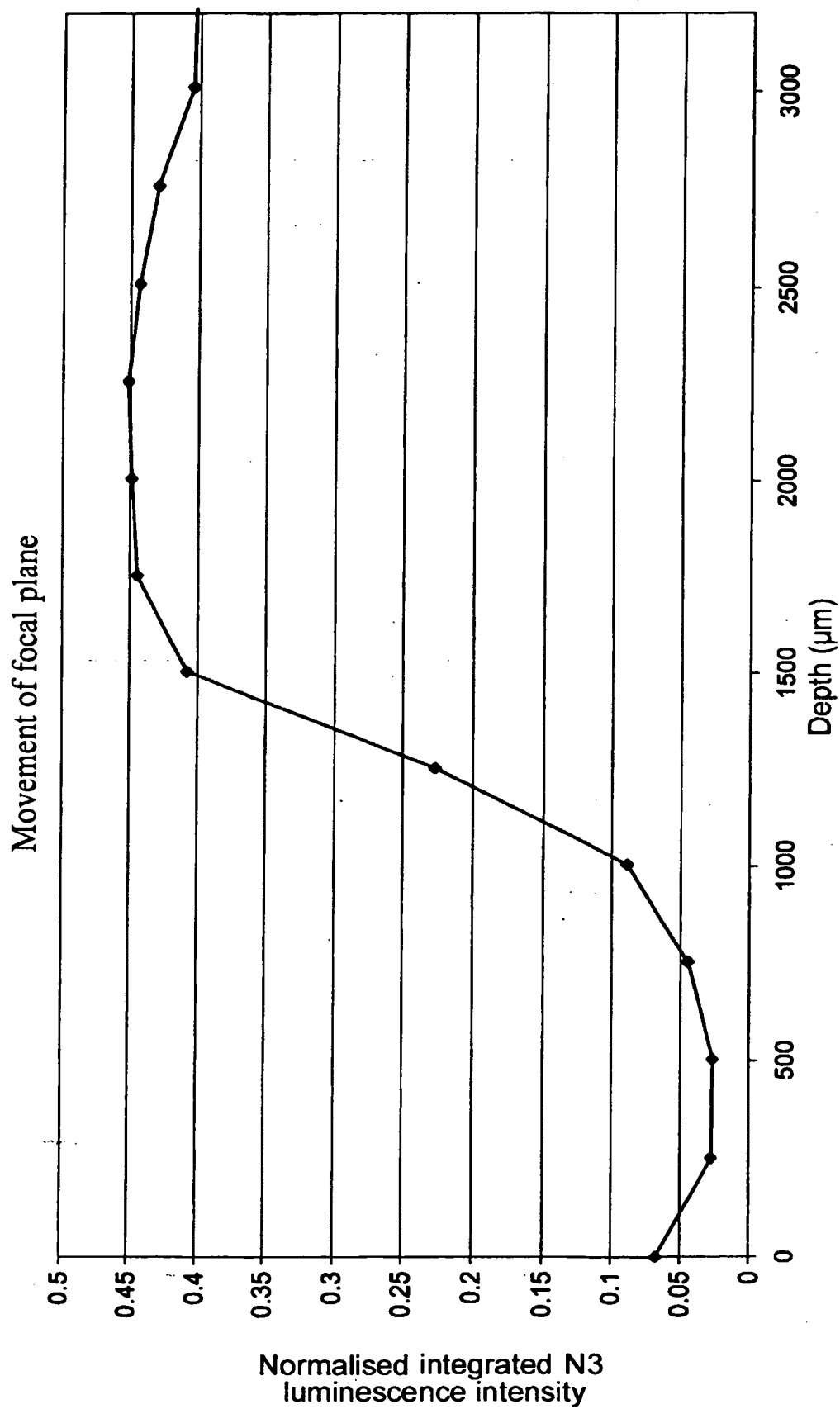


Fig.9b

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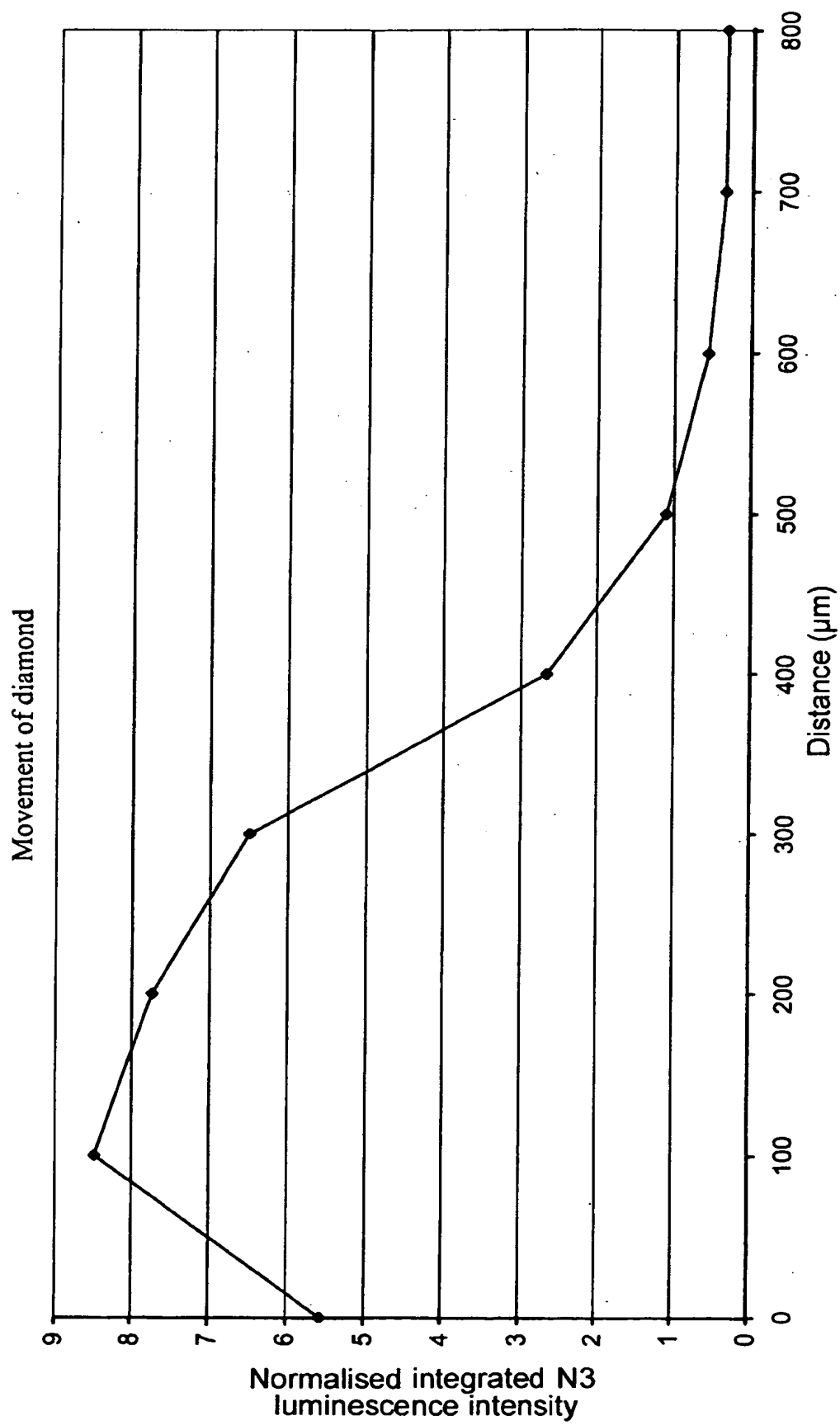


Fig.10a

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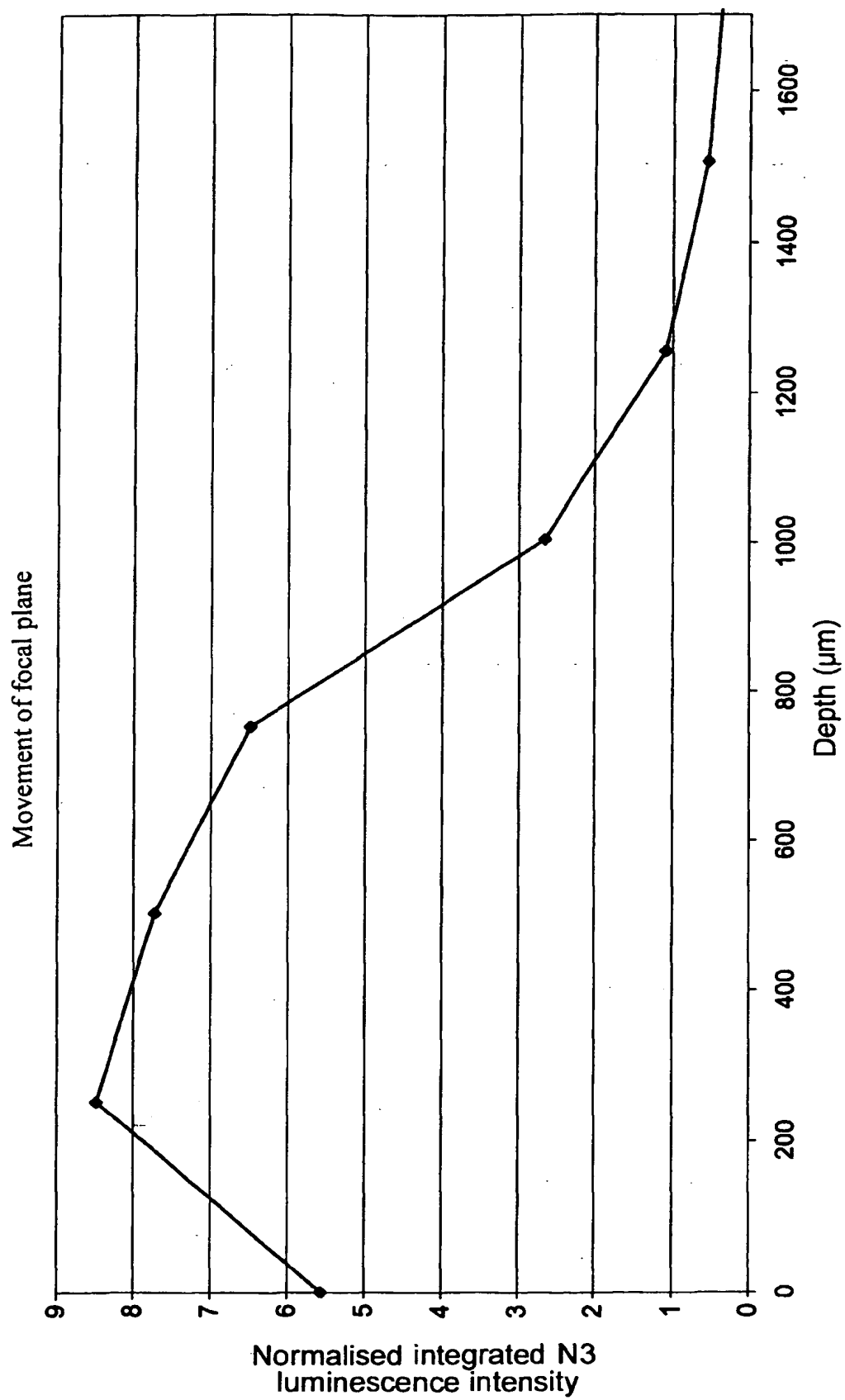


Fig.10b

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01N21/87

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PRAWER S ET AL: "Confocal Raman strain mapping of isolated single CVD diamond crystals" DIAMOND AND RELATED MATERIALS, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 7, no. 2-5, 1 February 1998 (1998-02-01), pages 215-221, XP004115037 ISSN: 0925-9635 figures 2,3	1-21,23
Y	US 6 014 208 A (SMITH JAMES GORDON CHARTERS ET AL) 11 January 2000 (2000-01-11) column 2, line 34 - column 3, line 15 column 6, line 18 - line 40 claims 16,35	1-21,23



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

22 November 2002

Date of mailing of the international search report

04/12/2002

Name and mailing address of the ISA

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Authorized officer

Consalvo, D

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/04146

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 883 389 A (SPEAR PAUL MARTYN ET AL) 16 March 1999 (1999-03-16) column 3, line 12 - column 4, line 64 ---	1-21,23
A	US 5 880 504 A (SMITH JAMES GORDON CHARTERS ET AL) 9 March 1999 (1999-03-09) column 4, line 26 - line 43 claims 1,2 ---	1-21,23
A	WO 99 57544 A (SPEAR PAUL MARTYN ; MARTINEAU PHILIP MAURICE (GB); GERSAN ETS (LI)) 11 November 1999 (1999-11-11) page 8, line 14 - line 27 -----	1-21,23

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 02/04146

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 22, 24
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 22,24

The subject-matter of claims 22 and 24 is unclear, does not contain technical features and does not comply with Rule 6.2 a) PCT.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 02/04146

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6014208	A	11-01-2000	GB 2303698 A	26-02-1997
			AU 702792 B2	04-03-1999
			AU 6527196 A	18-02-1997
			CA 2227472 A1	06-02-1997
			CN 1196120 A	14-10-1998
			EP 1158293 A2	28-11-2001
			EP 0840890 A1	13-05-1998
			WO 9704302 A1	06-02-1997
			GB 2317692 A , B	01-04-1998
			IL 118922 A	31-08-2000
			JP 11509629 T	24-08-1999
			RU 2175125 C2	20-10-2001
			TW 433463 Y	01-05-2001
			ZA 9606245 A	25-04-2000
US 5883389	A	16-03-1999	AU 676274 B2	06-03-1997
			AU 6146694 A	26-09-1994
			CA 2157469 A1	15-09-1994
			DE 69410242 D1	18-06-1998
			DE 69410242 T2	29-10-1998
			EP 0687356 A1	20-12-1995
			WO 9420837 A1	15-09-1994
			GB 2275788 A , B	07-09-1994
			HK 1006330 A1	19-02-1999
			IL 108871 A	08-02-1998
			JP 9505663 T	03-06-1997
			ZA 9401582 A	07-09-1994
US 5880504	A	09-03-1999	AU 698099 B2	22-10-1998
			AU 3395495 A	27-03-1996
			CA 2199359 A1	14-03-1996
			EP 0779978 A1	25-06-1997
			WO 9607896 A1	14-03-1996
			GB 2293236 A , B	20-03-1996
			IL 115209 A	14-07-1999
			JP 11511844 T	12-10-1999
WO 9957544	A	11-11-1999	ZA 9507480 A	06-03-1997
			GB 2336901 A	03-11-1999
			AU 3721799 A	23-11-1999
			WO 9957544 A1	11-11-1999